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**AN INVESTIGATION OF METHODS OF PRODUCING
SULFUR TRIOXIDE IN JET EXHAUSTS THROUGH ADDITION
OF FUEL ADDITIVES TO JP4**

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ABSTRACT

Work was performed to determine the possible effectiveness of sulfur-containing fuel additives as contrail suppressents. Such suppression would require production of significant levels of sulfur trioxide, a known suppressent, in the exhaust. A model combustor capable of simulating turbojet operation at 40,000 feet was designed and built, and a gas sampling and analysis procedure developed for measuring the concentration of sulfur trioxide. Organic fuel additives containing sulfur in various valence states were tested at many concentration levels, with and without the use of potentially catalytic co-additives such as nitrocompounds and organometallics. The level of sulfur trioxide in the exhaust was found to depend very little on the sulfur compound used, or its concentration above some threshold value, and the use of co-additives generally provided no improvement. The use of higher-valent sulfur compounds seems to have no advantage, and relatively low concentrations of inexpensive sulfur compounds, such as 0.5% carbon disulfide, merit operational testing. On the basis of limited data, the injection of sulfur dioxide into the intake air is significantly more effective than combustion of sulfur-containing fuels, and should also be investigated

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Work was performed to determine the possible effectiveness of sulfur-containing fuel additives as contrail suppressents. Such suppression would require production of significant levels of sulfur trioxide, a known suppressent, in the exhaust. A model combustor capable of simulating turbojet operation at 40,000 feet was designed and built, and a gas sampling and analysis procedure developed for measuring the concentration of sulfur trioxide. Organic fuel additives containing sulfur in various valence states were tested at many concentration levels, with and without the use of potentially catalytic co-additives such as nitrocompounds and organometallics. The level of sulfur trioxide in the exhaust was found to depend very little on the sulfur compound used, or its concentration above some threshold value, and the use of co-additives generally provided no improvement. The use of higher-valent sulfur compounds seems to have no advantage, and relatively low concentrations of inexpensive sulfur compounds, such as 0.5% carbon disulfide, merit operational testing. On the basis of limited data, the injection of sulfur dioxide into the intake air is significantly more effective than combustion of sulfur-containing fuels, and should also be investigated

as a possible basis for improved suppression systems. Measured yields of sulfur trioxide from the two recommended systems are 10 to 20% of the yield from current chlorosulfonic acid injection techniques, assuming complete conversion, but may lie much closer to actual values.

LIST OF CONTRIBUTORS

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I. INTRODUCTION

The work described in this Report represents a program devoted to the testing of a variety of sulfur-containing compounds as potential contrail-suppressent additives to kerosene-base turbojet fuels. The known suppressent action of chlorosulfonic acid injected into the post-combustion exhaust stream appears to confirm the hypothesis that sulfur trioxide and its hydrates should suppress the formation of visible contrails; the assumed mechanism of this suppression is discussed below. It follows that a successful sulfur-containing fuel additive can be operationally defined as one which leads to the formation of a level of sulfur trioxide in the exhaust which is comparable with that believed obtained by chlorosulfonic acid injection. The general program described here has consisted of selection of additives and co-additives for testing, construction of a combustor capable of burning kerosene-base fuel under conditions simulating an operational turbojet, development of a gas-sampling and analytic technique for determination of exhaust sulfur trioxide levels, and finally the actual testing of materials in various combinations and at various concentrations.

The desirability of a contrail suppression system for tactical aircraft is apparent. Contrails simplify the spotting of aircraft under conditions where they

might otherwise pass unobserved. These contrails are formed as a result of the condensation of water vapor ingested by the engine and vastly augmented by the combustion of a hydrocarbon fuel. Calculations indicate that autogenous condensation should not occur in the exhaust stream at the expected supersaturations. The actual condensation must therefore occur through heterogeneous nucleation involving atmospheric dust, salt particles, or engine ash, or alternatively in turbulent regions of locally high supersaturation. These mechanisms lead to fewer nuclei than would be the case if autogenous nucleation occurred, so that the resultant droplets are larger and in fact visible. If the droplets formed were typically smaller than 2500 angstroms, the exhaust would disperse light only by Rayleigh scattering, and the contrail would be visible, if at all, as a faint bluish haze.

An effective suppression system must lead to the formation of droplets below this size limit, which implies nucleation of at least 10^8 droplets per cubic centimeter. Present techniques achieve this level of nucleation by injection of chlorosulfonic acid; the resultant sulfur trioxide nucleates at a relatively high temperature (if indeed it ever completely vaporizes in the exhaust), and its highly hygroscopic character leads to the production of microdroplets of concentrated sulfuric acid which are effective

nuclei for condensation of water vapor. This system requires special equipment and the handling of a corrosive and hazardous liquid; a simpler and more maintenance-free system is desirable.

One such system would consist of the combustion of fuel containing soluble sulfur compounds. The difficulty here is that sulfur trioxide is not the equilibrium oxidation state of sulfur at temperatures over about 900°C , so that normal turbojet combustion would lead initially almost exclusively to sulfur dioxide. As the combustion gases cool, sulfur trioxide becomes the preferred form, but the rate of re-equilibration, in the absence of catalysis, is very slow. It is this combination of factors which requires the use of catalysts in the commercial production of sulfuric acid.

Two possible techniques for obtaining significant conversion to sulfur trioxide suggested themselves at the outset of this work. One was the use of organic sulfur compounds already in the +6 oxidation state (such as organic sulfates), since an appreciable amount of this hexavalent sulfur might well survive the very brief high-temperature combustion period; the other was the use of co-additives (such as nitro-compounds or organometallic compounds) which could be expected to lead to combustion products capable of catalyzing the conversion of sulfur dioxide to sulfur trioxide in the cooling exhaust.

Both of these techniques have been studied in the course of this contract.

II. COMBUSTOR DESIGN

For the actual combustion testing of additives, the need existed for a laboratory-scale combustor operable under conditions similar to those existing within an individual combustion chamber of a turbo-jet engine. It was decided to attempt simulation of an engine operating at 40,000 feet, an altitude at which contrails are encountered, and which requires a smaller air through-put than simulation of lower altitudes. The components of the combustor as constructed are shown in the photographs, Figure 1 through 4, and the assembly is shown schematically in Figure 5.

Figure 1 shows the combustor tail-pipe, the inner and outer combustion chamber liners, and the slip-ring bands which control primary and secondary air flow into the combustion region. One of the thermocouple leads, and the ceramic ignition system insulators, can also be seen. The inner liner and the slip-rings are made of inconel, and the other metallic components of the system are 316 stainless. Figure 2 shows the assembled system, including the Sutorbilt rotary positive displacement blower and its motor. This blower delivers 135 cubic feet of air per minute at pressures of about 1 psig. Measured pressures between the blower and the combustion chamber were only

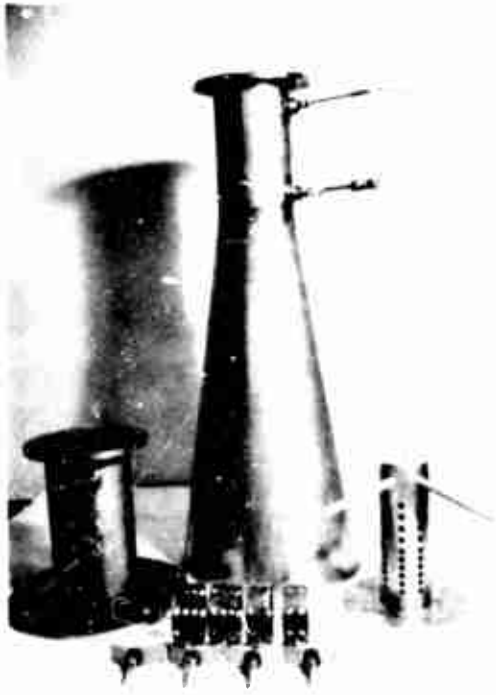


Figure 1

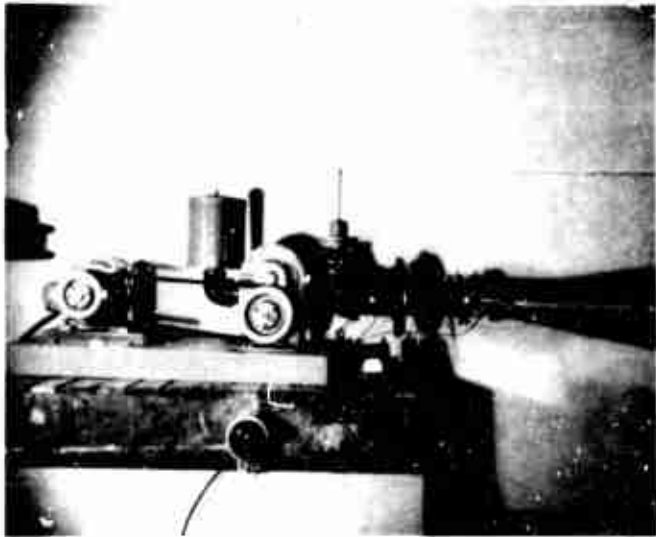


Figure 2

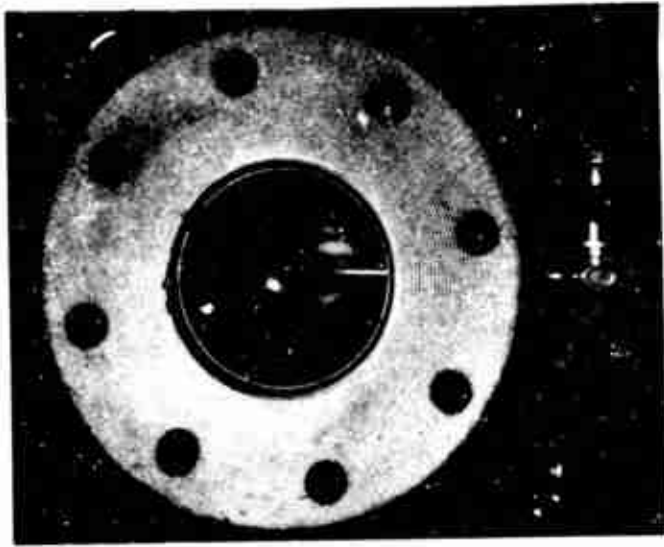


Figure 3

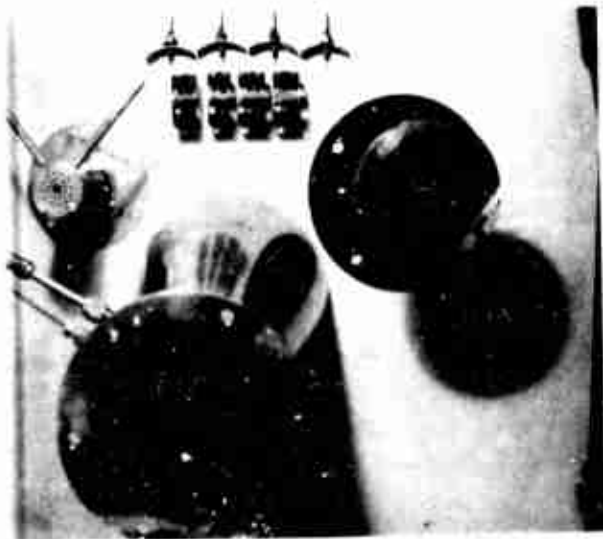


Figure 4

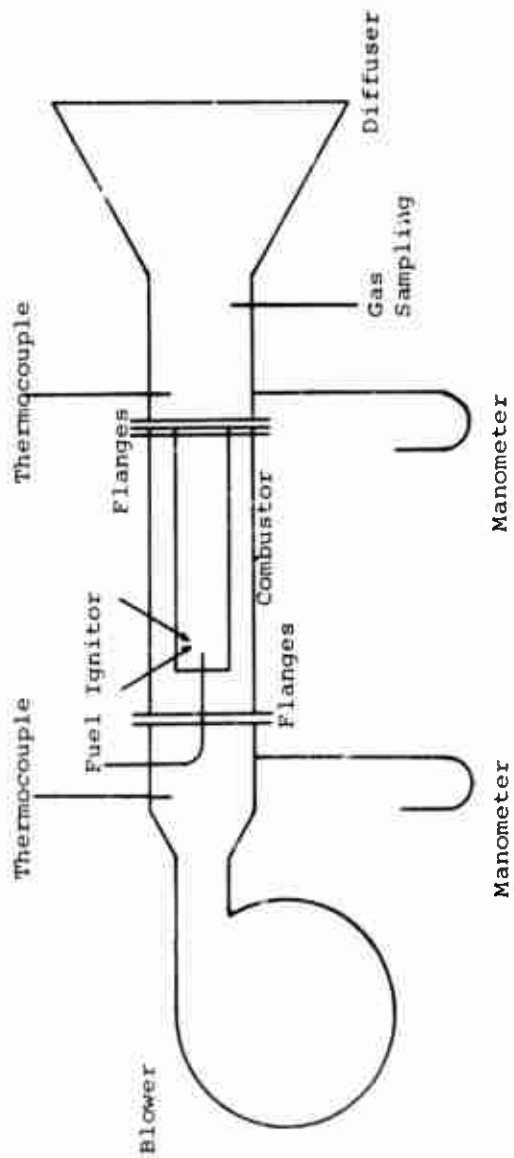


Figure 5
SCHEMATIC OF COMBUSTION CHAMBER ASSEMBLY

slightly above one atmosphere, and little compressive pre-heating of the air occurred; in an actual turbojet this preheating heats the air to about 220°C , but this difference was not expected to materially effect the adequacy of simulation. Figure 3 shows the fuel nozzle, specially constructed by Spray Engineering, as mounted at the forward end of the combustion chamber. This nozzle is smaller than any used in actual engines, and delivered 90 ± 20 mil per minute at fuel pressures between 50 and 150 psig, obtained with tank nitrogen. This nozzle, and a second nozzle obtained late in the contract, repeatedly clogged, even when protected with a fine-mesh stainless steel filter. This clogging could be cleared with chlorosulfonic acid, but became more frequent with the passage of time.

Figure 4 is another disassembled view of the major components, showing the face plate of the inner liner, and the position of the thermocouple and gas-sampling line within the tail-pipe.

Experimentation showed that optimum conditions prevail with all of the liner holes open for maximum air flow. Under these conditions the laboratory combustor has a combustion temperature of 1500°F to 1800°F and a gas residence time of 2.4 milliseconds, as compared with actual values in an engine at 40,000 feet of 1750°F and 2.0 milliseconds. Thus the model gives a slightly longer dwell time at a slightly

lower temperature. The small difference in temperature is accounted for by the lower compressive preheating in the model. Considering the over-all nature of combustor design technology, the attained simulation is very good.

III. GAS SAMPLING AND ANALYSIS

After consideration of various types of instrumental analysis of sulfur trioxide concentration in the exhaust stream, it was concluded that the most practical method for work of this scope would consist of a conventional wet chemical analysis of scrubbing solutions through which a known fraction of the exhaust had been drawn. The two key questions in this approach were whether a scrubbing system capable of handling a sufficient volume of exhaust gas, with a small volume of scrubbing liquid, could do an efficient job of scavenging sulfur trioxide (a notorious mist-former), and whether solutions obtained by such a technique would contain sufficient sulfate for routine analysis.

It soon became apparent that the requirement for handling a sufficient quantity of exhaust gas placed severe constraints on the form of scrubbing system used. It was calculated that a sampling rate of about 60 liters per minute would be required to obtain an adequate concentration of sulfate in about one half liter of scrubbing liquid, and this rate quite ruled out any elaborate glass-frit gas dispersion system,

although such systems were initially investigated while the analysis technique was under development. The final system consisted of about 150 ml of 4:1 isopropanol:water in each of three 2 liter filter flasks, each fitted with a half inch glass tube whose lower opening was beneath the surface of the liquid and bent nearly parallel with the bottom of the flask to promote swirling and good agitation during gas flow.

The neck of each flask was packed with glass wool to impede transfer of mist between flasks; the three flasks were connected in series and cooled during operation to improve the collection of sulfur trioxide and reduce evaporation; the first flask was cooled with dry ice/acetone and the others with ice. This cooling, by lowering the vapor pressure of the solvent, significantly reduced the formation of a sulfuric acid aerosol. The choice of an isopropanol:water solvent was based on information in the literature showing that isopropanol prevents the oxidative conversion of sulfite to sulfate in solution, and indeed storage of sulfate/sulfite solutions up to 48 hours gave no pronounced change in titer. Analysis of the collected sulfate was performed on the contents of all three flasks, and on washings from the glass wool plugs and tubing. Use of four flasks showed little sulfate in the last flask, so that three flasks were adopted as stand-

ard except on some early runs in which only two were used.

Two methods were employed for drawing sample gas through this scrubbing system. Initially the outlet from the last flask was connected back into the inlet to the filter on the Sutorbilt blower driving the combustor. This approach, used on early runs, recycled about 2% of the exhaust gas through the engine, and interfered somewhat with optimum operation. Subsequently a Hurricane Gas Sampler (a small high throughput commercial blower) was substituted, giving improved sampling rates and allowing better engine operation. In both cases the rate of gas sampling was determined by a tantalum-ball rotameter calibrated in our own laboratory, and was typically about 60 liters per minute at atmospheric temperature and pressure.

The analytic technique which was used to titrate the sulfate in aliquots from the flasks and washings is described by Fielder and Morgan, *Anal. Chim. Acta* 23 (1960), pp. 538-540, and the references given in that article. The titration uses barium ions (as barium perchlorate) to titrate sulfate, forming the very stable and insoluble barium sulfate. The end-point is determined using the indicator "Thoron" which changes from its normal yellow color in solution to a pale pink barium complex as soon as excess barium is present. This titration was found to be accurate to a fraction of a milligram of sulfate in about 100 ml of solution, using standard sulfate solutions pre-

pared by careful dilution, although the end-point color change is hard to observe at low concentrations. Typical combustor runs yield sulfate solutions ranging from over 30 mg in the first flask to a few tenths of a milligram in the third flask, so the sensitivity of the titration is adequate.

The use of standard sulfate solutions demonstrated the accuracy of the titration, but calibration of the efficiency of the scrubbing train was more difficult. The gradation between the amount of sulfate found in the first flask and that found in the last suggested good scavenging of sulfur trioxide, and the numbers given in the next section are reported on the assumption that recovery of sulfate is almost complete. Careful transfer of sulfur trioxide into isopropanol:water solution in the laboratory generally indicated about 90% recovery, and a 10% correction factor has been (somewhat arbitrarily) applied to the reported numbers.

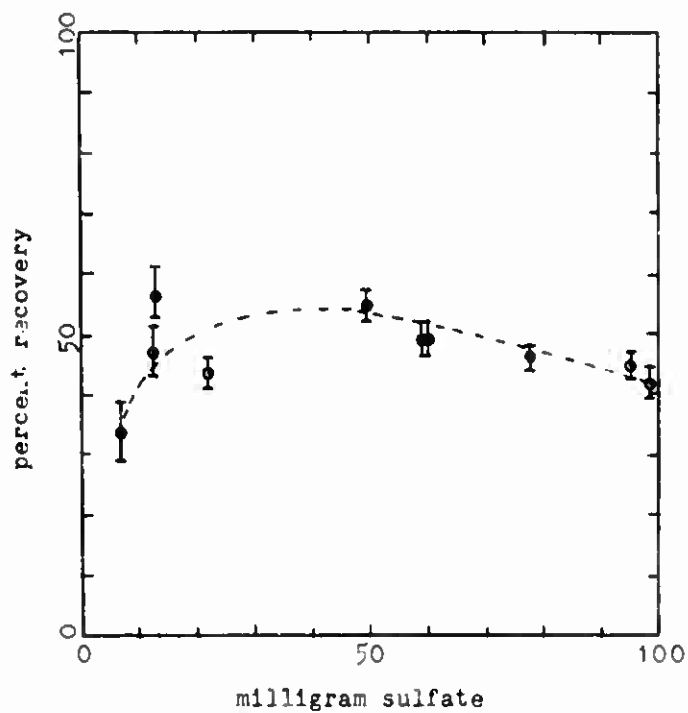
Clearly an improved calibration of the entire sampling and analysis system was called for and experiments to provide this information were performed toward the end of the research period. For this purpose the combustor was modified to allow injection of dry gaseous sulfur trioxide into the exhaust stream behind the combustion chamber. This sulfur trioxide was obtained by passing dry nitrogen through warm "fuming sulfuric acid" (a solution

of sulfur trioxide in sulfuric acid). This flow of nitrogen containing sulfur trioxide was maintained during operation of the combustor for a period of time similar to a typical additive run, both with and without an actual flame, and the total sulfur trioxide introduced was determined by the loss in weight of the sample of fuming sulfuric acid, quantitative transfer having been demonstrated previously by absorption on Ascarite. Quantities were used which bracket the amounts found in practice.

During these calibration runs the tail-pipe of the combustor was extended with a two foot length of 4" i.d. Transite pipe lined with stainless steel, and sample gas was withdrawn from the further end of this extension. The purpose of this extension was to allow adequate opportunity for mixing of the sulfur trioxide vapor with the exhaust stream, in order to ensure an authentic sample. This extension was left in the combustor during later additive runs.

The results of these experiments are shown in Figure 6, which is a plot of percent sulfur trioxide recovered versus the quantity introduced, with the latter being given in terms of the number of milligrams of sulfate expected to pass into the sampling system. The error bars represent as assumed $\pm 10\%$ system error coupled with a ± 1 gm weighing error in the fuming sulfuric acid. It can be seen that a broad maximum recovery is found near 35 mg, and that this maximum indicates about 55% recovery. This is

FIGURE 6 CALIBRATION CURVE BASED ON SULFUR TRI-
OXIDE INTRODUCTION



in the range of SO_3 recovery corresponding to operation of the combustor with fuel additives. In all of these calibration runs substantially more sulfate was found in the glass wool from the flasks than occurred during standard operation. This suggests that recovery was poorer during the calibrations than during combustion with fuel additives, perhaps because of a greater tendency for mist formation before the sulfur trioxide introduced for calibration had time to disperse to a uniform low concentration. In any case this remains an open question, and all that can be said is that recovery is almost certainly in the range between 50% and 100%. The factor-of-two correction indicated by Figure 6 has not been applied to the numbers reported in the next Section.

IV. SUMMARY OF RESULTS

Tests were conducted on a total of seven sulfur-containing additives (one of which was gaseous sulfur dioxide) and six co-additives with potential catalytic properties, at a total of thirty-one different combinations and concentrations. Ninety-two additive runs were made and analyzed, plus ten calibration runs involving injection of sulfur trioxide. Most runs were performed at least in duplicate or triplicate.

This body of data is presented in Table 1, and a word should be said here about the form of the

TABLE 1

<u>Additive</u>	<u>Co-additive</u>	<u>Gm(S)/L</u>	<u>Gm(S-VI)/L</u>	<u>Comments</u>
1) 2.5% Thiophene	None	10.0	0.48	
2)			0.60	
3)			0.48	
4)			0.54	
5) 5.0% Thiophene	None	20.1	0.77	Early Run
6)			0.99	Early Run
7)			1.18	Early Run
8)			1.09	
9)			1.04	
10)			0.81	Silica Wool Trap
11)			0.56	
12)			0.61	
13) 7.5% Thiophene	None	30.1	0.58	
14)			0.57	
15)			0.71	
16)			0.65	
17) 10.0% Thiophene	None	40.2	0.97	Silica Wool Trap
18)			0.62	
19)			1.14	
20)			0.86	Pyrex wool Trap
21)			0.94	
22)			0.49	
23)			0.59	
24)			0.53	
25)			0.61	

TABLE 1 (Continued)

<u>Additive</u>		<u>Co-additive</u>	<u>Gm(S)/L</u>	<u>Gm(S-VI)/L</u>	<u>Comments</u>
26)	5.0% Tetrahydro-	None	18.2	0.63	
27)	thiophene			0.62	
28)	10.0% Tetrahydro-	None	36.4	0.67	
29)	thiophene			0.55	
30)	0.5% Carbon Disul-	None	0.53	0.29	
31)	fide			0.30	
32)	2.6% Carbon Disul-	None	0.06	0.40	
33)	fide			0.40	
34)	0.5% Carbon Disul-	None	5.3	0.55	
35)	fide			0.63	
36)	2.0% Carbon Disul-	None	21.2	0.68	
37)	fide			0.77	
38)	4.0% Carbon Disul-	None	42.4	0.63	Double Run
39)	fide			0.74	
40)				0.57	
41)				0.59	
42)	8.0% Carbon Disul-	None	84.9	0.84	Steel Wool Trap
43)	fide			0.40	
44)				0.47	
45)				0.96	
46)				0.58	
47)				0.45	
					Stainless Steel Insert

TABLE 1 (Continued)

<u>Additive</u>		<u>Co-additive</u>	<u>Gm(S)/L</u>	<u>Gm(S-VI)/L</u>	<u>Comments</u>
48)	8.0% Carbon Disulfide	None	84.9	0.62	Stainless Steel Insert
49)				0.43	Stainless Steel Insert
50)				0.60	Stainless Steel Insert
51)				0.44	Holder in Flame
52)				0.55	Holder in Flame
53)				0.61	Stainless Steel Insert
54)				0.63	Inconel in Flame
55)				0.74	Holder in Flame
56)	16.0% Carbon Disulfide	None	169.8	0.70	
57)				0.59	
58)	5.0% Amyl Sulfate	None	ca. 7.0	0.19	Early Run
59)				0.14	Early Run
60)				0.09	
61)				0.23	
62)				0.10	
63)				0.14	
64)				0.19	
65)	5.1% Isoamyl Sulfone	None	ca. 8.0	0.54	
66)				0.59	
67)	5.0% Butyl Sulfite	None	ca. 8.5	0.58	
68)				0.53	
69)	2.5% Thiophene	5.0% Nitropropane	10.0	0.45	

TABLE 1 (Continued)

<u>Additive</u>		<u>Co-additive</u>	<u>Gm(S)/L</u>	<u>Gm(S-VI)/L</u>	<u>Comments</u>
70)	5.0% Thiophene	5.0% Nitropropane	20.1	2.26	Early Run
71)				0.91	Early Run
72)				0.38	
73)				0.45	
74)	5.0% Thiophene	5 ml Tetrabutyltin	20.1	0.81	
75)				0.55	
76)	5.0% Thiophene	10 ml Tetrabutyltin	20.1	0.56	
77)				0.43	
78)	5.0% Thiophene	5 gm Tetrabutyllead	20.1	0.38	Steel Wool Trap
79)				0.36	
80)	5.0% Amyl Sul-	5.0% Nitropropane	ca. 7.0	0.31	Early Run
81)	fate			0.23	
82)	5.0% Tetrahydro-	5.0% Nitropropane	18.2	0.45	
	thiophene				
83)	4.0% Carbon Di-	.25 gm Platinum(Ac) ₂ [*]	42.4	1.09	
84)	sulfide			0.53	Late Run
85)	4.0% Carbon Di-	0.1 gm Vanadyl(Ac) ₃ [*]	42.4	0.47	
	sulfide				
86)	4.0% Carbon Di-	Saturated "	42.4	0.43	
	sulfide				

TABLE 1 (Continued)

<u>Additive</u>	<u>Co-additive</u>	<u>Gm(S)/L</u>	<u>Gm(S-VI)/L</u>	<u>Comments</u>
87) 4.0% Carbon Di- 88) sulfide	0.1 gm Ferric(Ac) ₃ *	42.4	0.39 0.43	
89) 18.5 gm Sulfur Dioxide	None	9.25	0.42	Before Flame
90) 70.3 gm Sulfur Dioxide	None	35.1	1.88	Before Flame
91) 23.7 gm Sulfur Dioxide	None	11.8	0.59	After Flame
92) 54.5 gm Sulfur Dioxide	None	27.2	0.81	After Flame

* Ac = Acetylacetonate

presentation. Most runs were made with one liter of fuel, generally made up as a certain volume percent additive and co-additive when these were liquids, and by weight in the case of solids. This composition is indicated in the first and second columns. The third column gives the number of grams of sulfur actually present per liter of fuel, based on the percent sulfur in the additive and its specific gravity. The fourth column gives the number of sulfur per liter of fuel which was found to have emerged from the combustor as sulfur trioxide. This is a significant figure-of-merit; a number near 5.0 would represent a concentration of sulfur trioxide in the exhaust comparable to that theoretically obtained from present chlorosulfonic acid injection systems. The ratio of the numbers in column four to those in column three gives the percent conversion of sulfur to its trioxide in each case. The last column is reserved for comments on the individual runs. The comment "Early Run" indicates one of the first few runs in which less than three collection flasks were used, and operation was less well controlled. The comment "Late Run" refers to one of the last few runs, after evidence indicated that the combustor had been poisoned in some way and yields were reduced; this is discussed in the next Section. Comments referring to "Trap" (e.g., steel wool trap) point out those runs in which a filter was interposed between the

combustor and the first collection flask to stop possible fly-ash, and give the material used in the filter. Within each category in the Table, the listing is in chronological order. The comment "Double Run" refers to a run in which two liters of fuel plus additive were burned over twice the usual period of time. Other comments are explained in the next Section.

V. DISCUSSION AND CONCLUSIONS

The data presented in Table 1 lead at once to certain observations. Setting aside the early runs with less than three scrubbing flasks and incompletely developed procedures, there remains considerable scatter in the numbers obtained; within this scatter, the most notable tendency is the constancy of the "grams of hexavalent sulfur per liter" numbers, which quite generally lie in the range 0.55 ± 0.15 . This constancy, which covers additives of very different structure and extends over a concentration range of two orders of magnitude, strongly suggests that the mechanism leading to observed sulfur trioxide is zeroth order in its rate controlling step; indeed, formation of products at a rate which is independent of reactant concentration is the definition of a zeroth order reaction. Such zeroth order reactions are commonly associated with processes which occur only on walls or catalytic surfaces under conditions in which the available

surfaces are saturated. Since the most likely candidate for surface catalysis in the laboratory combustor was the metal surfaces near the combustion zone, runs 47 through 55 were made with various metal surfaces mounted directly in the combustion chamber exit. The runs marked "Stainless Steel Insert" were made with steel wool of high surface area, those marked "Holder in Flame" were made with a perforated stainless steel plate, and the inconel run was made with a sample of inconel turnings of moderately large surface. These runs did not show any marked change in sulfur trioxide yield.

The two concepts initially proposed as most promising, namely the use of hexavalent sulfur compounds and/or catalytic co-additives, likewise did not prove out. Amyl sulfate, with its absolute yield of about 0.2 grams of hexavalent sulfur per liter of fuel (about a 3% conversion of the sulfur in the additive to sulfur trioxide), was among the poorest additives studied. The sulfone and sulfite studied in runs 65 through 68 were much better than the sulfate, but no better than typical lower-valent sulfur compounds such as thiophene and carbon disulfide. The use of catalytic co-additives is covered in runs 69 through 88; compounds tested included nitropropane, a possible source of catalytic nitrogen oxides, and organometallic derivatives of Group IV metals, transition metals, and platinum. Only one of these runs gave a notably high absolute yield; this was the first test of 0.25 gm

of platinum diacetylacetonate in a liter of 4% carbon disulfide, and gave 1.09 grams of hexavalent sulfur per liter of fuel, not a high conversion, but an encouraging total amount. This system was not restudied until completion of the iron and vanadium tests, at which time studies with carbon disulfide with no co-additive showed that sulfur trioxide yields were down by about 40%. It must be assumed that one of the additives poisoned whatever surface was involved in sulfur trioxide formation, and time did not remain for remedial action. Thus the initial high value for the platinum compound may be correct; nevertheless economics preclude any practical application of such a system.

Runs 30 through 35 were made in an effort to determine just how low one could drop the total concentration of sulfur in the fuel without reducing the total output of sulfur trioxide. It had already been determined on several occasions that combustion of pure kerosene produced no sulfate titer in the scrubbing liquid. It can be seen from this data that when total sulfur in the fuel, present as carbon disulfide, is reduced to about 0.5 gm per liter, the yield of sulfur trioxide drops by about a factor of two from its limiting value at higher concentrations. At this level the percent conversion becomes quite large, exceeding 50%. It can also be seen that the use of 0.5 volume % carbon disulfide in kerosene gives about as much sulfur trioxide as the higher

concentrations. This would be an inexpensive and convenient fuel additive and should be considered for flight tests. It remains to be determined whether the amount of sulfur trioxide produced will be adequate for suppression.

To achieve the theoretical yield of sulfur trioxide from current chlorosulfonic acid injection systems, a value near 5.0 grams of hexavalent sulfur per liter of fuel is required. The carbon disulfide system mentioned above produces only about 11% of this amount. On the other hand the injection of chlorosulfonic acid is no doubt accompanied by some decomposition to sulfur dioxide, and it is possible that not all of the liquid acid is vaporized or dispersed sufficiently to participate in suppression. Moreover, the amount of chlorosulfonic acid used presently includes some margin, particularly since the amount of suppressant needed varies with altitude and humidity. Combining all of these factors with the uncertainty as to how much better (or worse) a carbon disulfide system might perform in actual operational turbojet engines, flight testing of 0.5% carbon disulfide is indicated.

The last data from Table 1 to deserve consideration are the final four runs with gaseous sulfur dioxide injection. These were made after the possible poisoning of the combustor, and may therefore be somewhat low. In any case the yield of 1.88 grams of sulfur in the form of the trioxide, obtained by

injecting 70 grams of dry sulfur dioxide into the intake airstream during the combustion of a liter of kerosene, is the highest absolute concentration of sulfur trioxide found for any system tested. This suggests that the sulfur compounds tested may function almost entirely by complete conversion to sulfur dioxide, followed by some process which converts a small portion of the dioxide into the trioxide. If this process occurs in certain regions of the combustion chamber, for example near the ports where secondary air enters, it is easy to see why sulfur dioxide entering with the secondary air might be more effective as a source of sulfur trioxide. This is only speculative; more research would be required to support or reject the notion, but in practical terms the use of a system for injecting sulfur dioxide into turbojet intakes would be much simpler than the injection of chlorosulfonic acid into the exhaust. Sulfur dioxide is inexpensive and easy to handle, and there would be a minimum of opportunity for interference with engine operation by corrosion or gumming. It therefore seems prudent to recommend this sulfur dioxide system, along with the carbon disulfide system already mentioned, for further study either in the laboratory or in flight tests.

In summary, it has been found that the use of higher-valent sulfur compounds as fuel additives seems to have no advantage over the use of lower-

valent compounds for the purpose of producing sulfur trioxide in the exhaust, and that the use of nitrogenous or organometallic co-additives does not generally improve yields of the trioxide. On the other hand, relatively low concentrations of inexpensive sulfur compounds such as 0.5% carbon disulfide offer as much promise as other systems, and merit operational testing. On the basis of limited data, the injection of sulfur dioxide into intake air appears significantly more effective than combustion of sulfur-containing fuels, and should be investigated as a possible basis for a contrail suppression system superior to the post-combustion injection of chlorosulfonic acid.

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13. ABSTRACT The possible effectiveness of sulfur-containing fuel additives as contrail suppressants was investigated by analysis of sulfur trioxide concentration in the exhaust from a model combustor. This specially constructed combustor simulated turbojet operation at 40,000 feet. Exhaust was analyzed by scrubbing a known fraction through cold isopropanol/water and titrating total sulfate with barium perchlorate. Sulfur trioxide production was found to depend very little on the concentration or composition of the additive. The best systems, recommended for further study, were 0.5% carbon disulfide, and injection of sulfur dioxide into intake air. These give sulfur trioxide levels which are 10 to 20% of those obtained with currently operational systems based on injection of chlorosulfonic acid into the exhaust, assuming that all of the sulfur in the chlorosulfonic acid becomes available as the trioxide. (Author)		

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